



(51) International Patent Classification:
C23C 18/12 (2006.01)

(21) International Application Number:
PCT/GB2011/001667

(22) International Filing Date:
1 December 2011 (01.12.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1020614.2 6 December 2010 (06.12.2010) GB

(71) Applicant (for all designated States except US): **CAMBRIDGE DISPLAY TECHNOLOGY LIMITED** [GB/GB]; Building 2020 Cambourne Business Park, Cambridgeshire CB23 6DW (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **KUGLER, Thomas** [DE/GB]; Cambridge Display Technology LTD, Building 2020 Cambourne Business Park, Cambridgeshire CB23 6DW (GB).

(74) Agent: **SHARP, Alan**; c/o IP Department, Cambridge Display Technology LTD, Building 2020 Cambourne Business Park, Cambridgeshire CB23 6DW (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ADHESION LAYER FOR SOLUTION-PROCESSED TRANSITION METAL OXIDES ON INERT METAL CONTACTS

(57) Abstract: An ammonium thio-transition metal complex is used as an adhesion promoter for immobilising temperature-stable transition metal oxide layers on an inert metal surface. The ammonium thio-transition metal complex comprises a transition metal selected from molybdenum, tungsten and vanadium, and is preferably ammonium tetrathiomolybdate. A precursor of the transition metal oxide is deposited on the inert metal surface by a solution-based process. The precursor is a dispersion or a dissolution of the transition metal oxide, transition metal oxide hydrate, ammonium salt of an acidic transition metal oxide hydrate or phosphoric acid-transition metal oxide complex in water or a phosphoric acid-transition metal oxide complex dissolved in a polar organic solvent.



WO 2012/076835 A1

Adhesion Layer for Solution-Processed Transition Metal Oxides on Inert Metal Contacts

Field of Invention

5 The present invention relates to use of an ammonium thio-transition metal complex as an adhesion promoter for immobilising temperature-stable transition metal oxide layers on an inert metal layer, a process for the formation of said temperature-stable transition metal oxide on an inert metal layer and in the provision of organic thin film transistors that have a temperature-stable transition metal oxide layer immobilised on a source and/or drain electrode thereof by use of an ammonium thio-transition metal complex as an adhesion promoter.

Background of the Invention

15 Transistors can be divided into two main types: bipolar junction transistors and field-effect transistors. Both types share a common structure comprising three electrodes with a semiconductive material disposed therebetween in a channel region. The three electrodes of a bipolar junction transistor are known as the emitter, collector and base, whereas in a field-effect transistor the three electrodes are known as the source, drain and gate. Bipolar junction transistors may be described as current-operated devices as the current between the emitter and collector is controlled by the current flowing between the base and emitter. In contrast, field-effect transistors may be described as voltage-operated devices as the current flowing between source and drain is controlled by the voltage between the gate and the source.

25 Transistors can also be classified as p-type and n-type according to whether they comprise semiconductive material which conducts positive charge carriers (holes) or negative charge carriers (electrons) respectively. The semiconductive material may be selected according to its ability to accept, conduct, and donate charge. The ability of the semiconductive material to accept, conduct, and donate holes or electrons can be enhanced by doping the material. The material used for the source and drain electrodes can also be selected according to its ability to accept and inject holes or electrons. For example, a p-type transistor device can be formed by selecting a semiconductive material which is efficient at accepting, conducting, and donating holes, and selecting a material for the source and drain electrodes which is efficient at injecting and accepting holes from the semiconductive material. Good energy-level

matching of the Fermi-level in the electrodes with the HOMO (Highest Occupied Molecular Orbital) level of the semiconductive material can enhance hole injection and acceptance. In contrast, an n-type transistor device can be formed by selecting a semiconductive material which is efficient at accepting, conducting, and donating
5 electrons, and selecting a material for the source and drain electrodes which is efficient at injecting electrons into, and accepting electrons from, the semiconductive material. Good energy-level matching of the Fermi-level in the electrodes with the LUMO (Lowest Unoccupied Molecular Orbital) level of the semiconductive material can enhance electron injection and acceptance.

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Transistors can be formed by depositing the components in thin films to form thin film transistors. When an organic material is used as the semiconductive material in such a device, it is known as an organic thin film transistor.

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Various arrangements for organic thin film transistors are known. One such device is an insulated gate field-effect transistor which comprises source and drain electrodes with a semiconductive material disposed therebetween in a channel region, a gate
electrode disposed adjacent the semiconductive material and a layer of insulating material disposed between the gate electrode and the semiconductive material in the
20 channel region.

An example of such an organic thin film transistor is shown in Figure 1. The illustrated structure may be deposited on a substrate (not shown) and comprises source and drain electrodes 2, 4 which are spaced apart with a channel region 6 located
25 therebetween. An organic semiconductor 8 is deposited in the channel region 6 and may extend over at least a portion of the source and drain electrodes 2, 4. An insulating layer 10 of dielectric material is deposited over the organic semi-conductor 8 and may extend over at least a portion of the source and drain electrodes 2, 4. Finally, a gate electrode 12 is deposited over the insulating layer 10. The gate electrode 12 is
30 located over the channel region 6 and may extend over at least a portion of the source and drain electrodes 2, 4.

The structure described above is known as a top-gate organic thin film transistor as the gate is located on a top side of the device. Alternatively, it is also known to provide the

gate on a bottom side of the device to form a so-called bottom-gate organic thin film transistor.

5 An example of such a bottom-gate organic thin film transistor is shown in Figure 2. In order to show more clearly the relationship between the structures illustrated in Figures 1 and 2, like reference numerals have been used for corresponding parts. The bottom-gate structure illustrated in Figure 2 comprises a gate electrode 12 deposited on a substrate 1 with an insulating layer 10 of dielectric material deposited thereover. Source and drain electrodes 2, 4 are deposited over the insulating layer 10 of dielectric material. The source and drain electrodes 2, 4 are spaced apart with a channel region 6 located therebetween over the gate electrode. An organic semiconductor 8 is deposited in the channel region 6 and may extend over at least a portion of the source and drain electrodes 2, 4.

15 The conductivity of the channel can be altered by the application of a voltage at the gate. In this way the transistor can be switched on and off using an applied gate voltage. The drain current that is achievable for a given voltage is dependent on the mobility of the charge carriers in the organic semiconductor in the active region of the device (channel between the source and drain electrodes). Thus, in order to achieve high drain currents with low operational voltages, organic thin film transistors must have an organic semiconductor which has highly mobile charge carriers in the channel.

Charge carrier mobility is a measure of how easily a carrier moves in a particular material. This property of an organic semiconductor is, however, often compromised by the contact resistance of an organic thin film transistor device. A higher contact resistance results in a higher proportion of the applied voltage dropping across the interfaces between the source and drain electrodes and the organic semiconductor material in the transistor channel region and, as a result, a lower bias across the channel region is achieved. A high contact resistance thus has the effect of a much lower current level being extracted from the device due to the lower bias across the channel region, which comprises the charge carrier mobility of the organic semiconductor material.

Conventionally, contact resistance in organic transistors is reduced by applying surface treatment layers to the source and drain electrodes prior to depositing the

semiconductor film or changing metal to a higher work function as necessary to inject charges to the HOMO level (for a p-type material). Such treatment layers (typically self assembled monolayers applied from solution or vapour phase) are used to produce a dipole layer at the metal surface to effectively shift the work function of the source and drain contacts to align with the HOMO level in the semiconductor and therefore reduce the barrier for charge injection from metal to the semiconductor.

The range of electronic properties found amongst the transition metal oxides mean that they are particularly advantageous materials for controlling the work function and hence the charge-injection properties of an organic thin-film transistor (OTFT). WO 2007/005618 discloses the insertion of thin layers of transition-metal oxide such as MoO₃ between the organic semiconductor layer and the source and/or drain contacts in OTFTs. This prior art document, however, uses thermal evaporation to deposit the transition metal oxide. This has considerable disadvantages in terms of its potential for increasing up to a commercial scale process as it is both costly and inefficient.

Although transition metal oxides exhibit advantageous properties when deposited on the surfaces of source and drain electrodes of OTFTs, they do not adhere very well thereto.

Since source and drain electrodes must have the ability to accept and inject holes or electrons, they are usually fabricated from metallic conductors such as copper, silver or gold. Gold in particular is used for high-quality surface-to-surface contacts. These materials are, however, fairly unreactive. Pure gold is a chemically unreactive metal, whilst silver and copper surfaces react easily in air to form an unreactive metal oxide surface. Hence the source and drain electrode surfaces do not chemically react with the transition metal oxide layer deposited thereon. Significantly, these issues with adhesion can result in a non-uniform or even a discontinuous layer of transition metal oxide being deposited, making it extremely difficult to obtain repeatable results with the OTFTs. Thus whilst a transition metal oxide can improve contacts between the electrodes and active layers of an OTFT, its poor adhesion to the source and drain electrode surfaces when deposited thermally according to the prior art can limit the performance thereof.

There is thus a need to find an improved way of depositing transition metal oxide layers on inert metal layers. We have surprisingly found that it is possible to overcome the problems associated with metal oxide layers deposited by a thermal evaporation process according to the art by using an ammonium thio-transition metal complex as an adhesion promoter to immobilise transition metal oxides onto inert metal surfaces. The motivation for using such a complex is primarily to overcome the poor adhesion between the source and drain electrode surfaces and the transition metal oxide layer. This complex enables the formation of a continuous layer of transition metal oxide where the underlying substrate is made of an inert metal such as gold, onto which the transition metal oxide layer does not adhere well.

There are no examples of these complexes being used as adhesion promoters for organic thin-film transistors in the prior art. Rather the focus of the prior art is on improving the intrinsic electrical properties of the organic semiconductor layer within the OTFT and towards the development of device fabrication techniques ("High mobility solution processed 6,13-bis(triisopropyl-silylethynyl) pentacene organic thin film transistors"; S.K. Park et al., APPLIED PHYSICS LETTERS 91, 063514 (2007); Henning Sirringhaus, Takeo Kawase, Richard H. Friend, Tatsuya Shimoda, M. Inbasekaran, W. Wu, and E. P. Woo; "High-resolution inkjet printing of all-polymer transistor circuits", Science, 290, 2123-2126 (2000)). There has been no research published into the use of an adhesion promoter to immobilise a transition metal oxide layer onto the source and drain electrodes of an OTFT device.

Moreover adhesion of substrate layers in organic thin-film transistors is a crucial property to optimise because of the effect of poor adhesion on the performance of the device. There is therefore a need to find additional ways of improving the adhesion of transition metal oxide layers to inert metal surfaces in organic thin-film transistors. The present invention addresses this need.

Summary of the Invention

We have surprisingly discovered that an ammonium thio-transition metal complex adhesion promoter enables the deposition of a continuous layer of transition metal oxide onto an inert metal surface such as gold. This adhesion promoter enables the deposition of a temperature-stable transition metal oxide layer onto the source and/or drain electrode surface within an organic thin-film transistor using solution deposition techniques to produce ohmic contacts between the organic semiconductor layer and the source and/or drain electrodes. This thus overcomes the disadvantages of thermal deposition of transition metal oxides described in the art. In particular the thermal deposition techniques of the prior art involve the use of shadow masks, which renders scaling-up of the process to large substrate sizes difficult in case of high resolution patterns. In contrast, the process of the present invention enables the use of solution-based processes that can easily be scaled up to large substrate sizes in both a cost-effective and efficient manner.

Thus, in a first aspect of the present invention (1) there is provided use of an ammonium thio-transition metal complex as an adhesion promoter for immobilising temperature-stable transition metal oxide layers on an inert metal surface.

Preferred uses according to the present invention include:

- (2) use according to (1) wherein the ammonium thio-transition metal complex comprises a transition metal selected from molybdenum, tungsten and vanadium;
- (3) use according to (1) or (2) wherein the ammonium thio-transition metal complex is a tetrathio-transition metal complex;
- (4) use according to (3) wherein the ammonium tetrathio-transition metal complex is ammonium tetrathiomolybdate;
- (5) use according to any one of (1) to (4) wherein the transition metal oxide is MoO_3 , WO_3 or V_2O_5 ;

- (6) use according to any one of (1) to (5) wherein a precursor of the transition metal oxide is deposited on the inert metal surface by a solution-based process;
- 5 (7) use according to (6) wherein the precursor is a dispersion or a dissolution of the transition metal oxide, transition metal oxide hydrate, ammonium salt of an acidic transition metal oxide hydrate or phosphoric acid-transition metal oxide complex in water or a phosphoric acid-transition metal oxide complex dissolved in a polar organic solvent;
- 10 (8) use according to (7) wherein the transition metal oxide to be deposited is MoO_3 and the precursor is a dispersion or a dissolution of molybdenum trioxide, molybdic acid, ammonium molybdate or phosphomolybdic acid in water, or phosphomolybdic acid dissolved in a polar organic solvent;
- 15 (9) use according to (7) wherein the transition metal oxide to be deposited is WO_3 and the precursor is a dispersion or a dissolution of tungsten trioxide, tungstic acid, ammonium tungstate or phosphotungstic acid in water, or phosphotungstic acid dissolved in a polar organic solvent;
- 20 (10) use according to (7) wherein the transition metal oxide to be deposited is V_2O_5 and the precursor is a dispersion or a dissolution of vanadium (V) oxide, ammonium metavanadate, vanadium(V) oxytriethoxide vanadium(V) oxytriethoxide, vanadium(V) oxytriisopropoxide or vanadium(V) oxytripropoxide dissolved in a polar organic solvent;
- 25 (11) use according to any one of (6) to (10) wherein the solution-based process consists of spin-coating, dip-coating or inkjet-printing;
- 30 (12) use according to any one of (1) to (11) wherein the inert metal is silver, gold, or copper;
- (13) use according to (12) wherein the inert metal is gold; and

- (14) use according to any one of (1) to (13) wherein the transition metal oxide layer immobilised on the ammonium thio-transition metal complex is stable up to temperatures of at least 140°C.

5 We have also discovered that after deposition of an ammonium thio-transition metal complex onto an inert metal surface, solution-based processing of the transition metal oxide thereon produces a temperature-stable transition metal oxide layer. Solution-based processing of the transition metal oxide enables the use of simple and cost-effective solution deposition techniques such as spin-coating, dip-coating or ink-jet
10 printing. In contrast to thermal evaporation, solution-based deposition techniques do not require vacuum, and can therefore easily be scaled-up to large substrate sizes and/or reel-to-reel fabrication processes.

Thus in a second aspect of the present invention there is provided:

15

- (15) a process for forming a transition metal oxide on an inert metal surface comprising:
- (a) pre-treating the metal surface with an ammonium thio-transition metal complex;
 - 20 (b) depositing a solution comprising a transition metal oxide precursor onto the pre-treated surface; and
 - (c) annealing the deposited solution to form a layer of transition metal oxide.

25 Preferred aspects of the second aspect of the invention include:

- (16) a process according to (15) wherein step (a) comprises:
- (i) cleaning the metal surface to remove organic contaminants;
 - (ii) depositing the ammonium thio-transition metal complex onto the metal
30 surface; and
 - (iii) annealing of the treated surface in air;
- (17) a process according to (16) wherein the metal surface is cleaned by a UV-ozone treatment or an oxygen plasma treatment; and

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- (18) a process according to any one of (15) to (17) wherein the solution-based deposition is conducted by spin-coating, dip-coating or inkjet printing.

One preferred use of the deposition of a temperature-stable transition metal oxide layer promoted using an ammonium thio-transition metal complex in accordance with the present invention is in the fabrication of an organic thin-film transistor device by use of an ammonium thio-transition metal complex on the source and/or drain electrodes thereof before deposition of the transition metal oxide layer. Significantly this results in the fabrication of ohmic contacts between the organic semiconductor layer and the source and/or drain electrodes of the device.

Thus, in a third aspect of the present invention there is provided:

- (19) an organic thin-film transistor comprising source and drain electrodes, a gate electrode and an organic semiconductor layer, wherein the source and drain electrodes comprise an inert metal on which a temperature-stable transition metal oxide layer is immobilised by use of an ammonium thio-transition metal complex as an adhesion promoter.

Preferred aspects of the third aspect of the present invention include:

- (20) an organic thin-film transistor according to (19) wherein the transition metal oxide is immobilised according to the process defined in any one of (15) to (18) above;
- (21) an organic thin-film transistor according to (19) or (20) wherein the ammonium thio-transition metal complex is as defined in any one of (1) to (4) above; and
- (22) an organic thin-film transistor according to any one of (19) to (21) wherein the transition metal oxide is MoO_3 , WO_3 or V_2O_5 .

Detailed Description of the Invention

As explained above, we have discovered that the use of an adhesion promoter is an excellent means of producing a temperature-stable transition metal oxide layer on an inert metal surface. By using an adhesion promoter such as an ammonium thio-
5 transition metal complex the resulting transition metal oxide layer has a more stable work function when subjected to high temperatures compared to an inert metal surface without an adhesion promoter.

For example, the work function of an ammonium tetrathiomolybdate pre-treated gold
10 surface with molybdic acid deposited thereon is substantially more stable at temperatures up to 140°C, compared to the work function of a UV-ozone cleaned gold surface with molybdic acid deposited thereon without the pre-treatment. The stability of the work function is particularly advantageous in an organic thin-film transistor device where the temperature-stable transition metal oxide layer immobilised using the
15 ammonium thio-transition metal complex can be used to dope the interface between the source and/or drain electrodes and the organic semiconductor layer, thereby forming ohmic contacts at these interfaces.. Consequently, the contact resistance at the interfaces between the source/drain contacts and the organic semiconductor in the transistor channel is minimised, reducing the barrier for charge injection from metal to
20 semiconductor and resulting in a high performance organic thin-film transistor.

Preferred adhesion promoters are thio-transition metal complexes. These comprise complexes of a transition metal having at least one thio-transition metal bond. Particularly preferred are ammonium thio-transition metal complexes, for example
25 ammonium tetrathiomolybdate.

The transition metal of the ammonium thio-transition metal complex is preferably selected from the group consisting of molybdenum, tungsten, and vanadium. Particularly preferred complexes include molybdenum (Mo) or tungsten (W).
30

The term "inert metal" is used herein to encompass any metal which does not allow for good adhesion of a transition metal oxide onto the metal surface. These metals do, however, allow good adhesion of the thio-transition metal complexes used in the present invention to the surface thereof. It is believed that this property of sulphur in
35 the metal-thio bond in allowing adhesion on the inert metal surfaces is what allows the

ammonium thio-transition metal complex to act as an adhesion promoter for the transition metal oxide layer.

5 Preferred inert metals for use in the invention are gold, silver or copper. A particularly preferred metal is gold.

10 The transition metal oxide used in accordance with the present invention is deposited by means of a solution-based process. More preferably a precursor of the transition metal oxide is deposited by means of a solution-based process. The solution-based process can consist of spin-coating, dip-coating, inkjet-printing or any technique known to the skilled man comprising the deposition of material from a solution onto a surface.

15 The term "precursor" as used herein refers to a dispersion or a dissolution of a transition metal in solution. A preferred precursor is a dispersion or a dissolution of a transition metal oxide, transition metal oxide hydrate, ammonium salt of an acidic transition metal oxide hydrate or phosphoric acid-transition metal oxide complex in water or a phosphoric acid-transition metal oxide complex dissolved in a polar organic solvent.

20 Examples of precursors which could be used in accordance with the current invention for deposition of molybdenum trioxide include a dispersion or dissolution of any of the following compounds in water: molybdenum trioxide, molybdic acid, ammonium molybdate or phosphomolybdic acid; or the dispersion or dissolution of a heteropolyacid in a polar organic solvent such as poly phosphomolybdic acid.

25 For the deposition of tungsten trioxide the preferred precursor is a dispersion or a dissolution of any of the following compounds in water: tungsten trioxide, tungstic acid, ammonium tungstate or phosphotungstic acid; or the dispersion or dissolution of a heteropolyacid in a polar organic solvent such as phosphotungstic acid.

30 For the deposition of vanadium pentoxide the preferred precursor is a dispersion or a dissolution of any of the following compounds in water: vanadium (V) oxide, ammonium metavanadate, vanadium (V) oxytriethoxide, vanadium (V) oxytriisopropoxide or vanadium (V) oxytripropoxide; or a dispersion or a dissolution of a heteropolyacid in a polar organic solvent such as vanadium (V) oxytriethoxide, vanadium (V)

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oxytriisopropoxide or vanadium (V) oxytripropoxide. Possible organic solvents include pyridine, acetonitrile, tetrahydrofuran or any other polar organic solvent known to the skilled man.

- 5 The deposited transition metal oxide in accordance with the present invention encompasses any transition metal oxide in which the metal cations assume a high oxidation state and are capable of p-doping the organic semiconductor material in the transistor channel. Preferably the transition metal oxide is an oxide of molybdenum, tungsten or vanadium, more preferably an oxide of molybdenum. Preferred transition
10 metal oxides are selected from the group consisting of MoO_3 , WO_3 or V_2O_5 , most preferably MoO_3 .

The resulting transition metal oxide layer is temperature-stable. Stability is preferably measured by the surface work function at temperatures up to at least 140°C , preferably
15 at temperatures up to 170°C , and more preferably at temperatures up to 200°C .

The process of the invention involves the formation of an insulating transition metal oxide on an inert metal surface. This process typically involves pre-treatment of the surface with an adhesion promoter, deposition of a transition metal oxide precursor and
20 annealing to form a transition metal oxide layer. The adhesion promoter, precursor, the deposition process of the precursor and the transition metal oxide are as hereinbefore defined. The annealing process to form a transition metal oxide layer is preferably carried out at a temperature between 120 to 250°C .

25 Preferably pre-treatment of the inert metal surface comprises:

- (i) cleaning the metal surface;
- (ii) depositing an ammonium thio-transition metal complex onto the metal surface; and
- (iii) annealing of the treated surface in air.

30

The cleaning step of the process according to the current invention consists of any treatment which removes organic contaminants. Preferably the inert metal surface is cleaned by a UV-ozone treatment or an oxygen plasma treatment. Particularly preferred is a UV-ozone treatment. By such an oxidative cleaning process, the metal
35 surface is rendered hydrophilic and its surface work function increased. Using a gold

surface treated with UV-ozone as an example, the surface work function increases to approximately 5.6eV and the gold surface is rendered hydrophilic.

5 Deposition of an ammonium thio-transition metal complex onto the cleaned metal surface is preferably via a solution-based process. The solution used is preferably a solution of the ammonium thio-transition metal complex in water, the concentration depending on the solubility of the ammonium thio-transition metal complex in water (e.g. a 0.5% (w/w) solution), and after deposition the pre-treated surface is dried by any means known to the skilled man. It is found that the pre-treated surface typically has a
10 lower work function compared to the cleaned metal surface described above. Using ammonium tetrathiomolybdate in water as an example, when the substrate is immersed in a 0.5% (w/w) solution of ammonium tetrathiomolybdate in water and then blow-dried with a nitrogen gun, this pre-treatment decreases the surface work function to approximately 4.6eV.

15 Drying or annealing of the treated surface in air is preferably carried out at a temperature between 120 to 250°C. Particularly preferred is drying of the treated surface at a temperature towards the lower end of this range (e.g. 120°C to 150°C) for a period of time (e.g. 5 to 20 minutes), followed by annealing of the treated surface at a
20 temperature towards the higher end of this range (e.g. 150°C to 250°C) for a period of time (e.g. 5 to 30 minutes). Annealing of the treated surface in air is generally found to result in an increase of the surface work function. Using an ammonium tetrathiomolybdate pre-treated gold substrate as an example, the surface is first dried at 125°C for 5 minutes and then annealed at 175°C for 10 minutes. The surface work
25 function correspondingly increases from 4.6eV to 4.95eV and then 5.1eV.

The deposition of the precursor of a transition metal oxide is preferably by a solution-based process in which the ammonium thio-transition metal complex pre-treated surface is immersed in a dispersion or a dissolution of the transition metal oxide, transition metal oxide hydrate, ammonium salt of an acidic transition metal oxide
30 hydrate or phosphoric acid-transition metal oxide complex in water or a phosphoric acid-transition metal oxide complex dissolved in a polar organic solvent, and then dried using any means known to the skilled man. The deposition of the precursor typically increases the surface work function. Using an ammonium tetrathiomolybdate pre-
35 treated gold substrate and the deposition of molybdenum (IV) oxide thereon as an

example, the substrate was immersed in a 2% (w/w) solution of molybdic acid in water and then blown-dry with a nitrogen gun. The surface work function increased to 5.43eV from 4.8eV.

5 Alternatively the molybdic acid solution could have been applied by spin-coating or using an additive process such as inkjet printing. If inkjet printing is used, the spatial resolution of this process is preferably increased by using surface energy patterns to prevent the aqueous molybdic acid solution from spreading from the hydrophilic inert metal patterns onto the substrate.

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After application of the precursor of a transition metal oxide onto the ammonium thio-transition metal complex pre-treated substrate, the precursor is converted to the transition metal oxide by thermal annealing. Annealing is preferably carried out between 120 to 200°C. Preferably the surface is dried at a temperature towards the lower end of this range for a period of time and then annealed at a temperature
15 towards the higher end of this range for a period of time. Upon annealing we have found that the surface work function remains stable. Using molybdic acid on an *ammonium tetrathiomolybdate* pre-treated gold surface as an example, the surface was dried at 120°C for 5 minutes and then annealed at 140°C for 5 minutes. The
20 surface work function remained stable up to 140°C at a value of approximately 5.4eV.

The organic thin film transistors according to the invention may be any organic thin film transistor that comprises an organic semiconductor layer. The transistors can be p-type or n-type. Suitable transistor configurations include top-gate transistors and
25 bottom-gate transistors. One preferred example of the uses and processes according to the invention is in the preparation of an organic thin film transistor comprising source and drain electrodes, a gate electrode and an organic semiconductor layer, wherein the source and drain electrodes comprise an inert metal on which a temperature-stable transition metal oxide layer is immobilised by use of an ammonium thio-transition metal
30 complex as an adhesion promoter. Both the transition metal oxide layer and the ammonium thio-transition metal complex are as hereinbefore defined.

By using an ammonium thio-transition metal complex as hereinbefore defined a temperature-stable transition metal oxide can be deposited onto the inert metal surface
35 of the source and drain contacts of the OTFT by a process described above. The

present invention therefore makes it possible to use a transition metal oxide layer to dope the interface between the source and drain contacts and the organic semiconductor layer, thereby creating an Ohmic contact in a stable, simple and cost effective manner. Further, the solution-based process for deposition of said layer in accordance with the process of the present invention is scalable up to large substrate sizes, making it far more practical for industrial application than prior art processes.

The present invention may be further understood by consideration of the following examples with reference to the following drawings.

Brief Description of the Figures

Figure 1 shows a typical top gate thin film transistor.

Figure 2 shows a typical bottom gate thin film transistor.

Figure 3 is a photoelectron spectrum recorded with an AC-2 spectrometer of photoelectron yield against photon energy measured for gold source and drain contacts at various stages during the deposition of ammonium tetrathiomolybdate thereon according to the present invention.

Figure 4 is a photoelectron spectrum recorded with an AC-2 spectrometer of photoelectron yield against photon energy measured at various stages for gold source and drain contacts pre-treated with an ammonium thiomolybdate adhesion layer during deposition of Mo-Acid thereon and annealing thereof to give a layer of molybdenum oxide according to the present invention.

Measurement of energy values with the AC-2 spectrometer

The energy level values plotted in Figures 3 and 4 were measured using the AC-2 photoelectron spectrometer available from RK Instruments Inc. The measurements were performed in air by probing a sample that was typically several square millimetres in area, and included the following steps:

- UV photons emitted from a deuterium lamp were monochromatised through the grating monochromator;
- the monochromatised UV photons were focused on a sample surface in the air;

- the energy of UV photon was increased from 3.4eV to 6.2eV, step by step;
- when the energy of the UV photon was higher than the threshold energy of photoemission of the sample material (i.e. the Ionisation Potential), the photoelectrons were emitted from the sample surface;
- 5 • photoelectrons emitted from the sample were then detected and counted in the air by the open counter; and
- the photoemission threshold (Ionisation Potential) was determined from the energy of an intersecting point between a background line and the extended line of the square root of the photoelectric quantum yield.

10

Examples

The following examples focus on the process of forming a transition metal oxide on an inert metal surface using an ammonium tetrathiomolybdate adhesion promoter to
15 obtain a temperature-stable organic thin-film transistor (OTFT) device as an example of the present invention.

Example 1

(a) **Pre-treatment of gold source and drain contacts by application of 20 ammonium tetrathiomolybdate**

The objective of these experiments was to pre-treat the inert surface of gold source and drain contacts by application of ammonium tetrathiomolybdate.

I. UV-ozone cleaning

25 An OTFT substrate comprising gold source and drain contacts on a glass substrate was treated with UV-ozone. In addition to partially removing organic contaminants, the UV-ozone treatment was found to increase the work function of the gold contacts to approximately 5.6eV and rendered the gold surface hydrophilic. This change in work function of the surface is shown in Figure 3 by the label (I).

30

II. Adsorption of ammonium tetrathiomolybdate

The UV-ozone treated OTFT substrate was then immersed in a 0.5% (w/w) solution of ammonium tetrathiomolybdate in water and blow-dried with a nitrogen gun.

The adsorption of ammonium tetrathiomolybdate resulted in a decrease of the surface work function of the gold contacts to 4.6eV. This is shown in Figure 3 by the label (II).

III. Annealing in air

5 The pre-treated gold contacts were then dried in air at 125°C for 5 minutes and then annealed in air at 175°C for 10 minutes. This annealing of the surface resulted in a gradual increase of the surface work function first to 4.95eV and then to 5.1eV. This is shown in Figure 3 by the label (III).

10

IV. Thermal decomposition in air

Finally the pre-treated gold contacts were annealed in air at 220°C for 10 minutes. This resulted in a strong decrease of the surface work function to 4.8eV. This is shown in Figure 3 by the label (IV).

15

(b) Application of molybdic acid

The ammonium tetrathiomolybdate pre-treated OTFT substrate was then immersed in a 2% (w/w) solution of molybdic acid in water, and blown-dry with a nitrogen gun.

20 The molybdic acid solution could also have been applied by spin-coating or by means of an additive process such as inkjet printing. In order to increase the spatial resolution of inkjet printing, surface energy patterns could be used to prevent the aqueous molybdic acid solution from spreading from the hydrophilic gold patterns onto the substrate. Such surface energy patterns could be pre-defined using photolithography.

25

(c) Conversion of deposited molybdic acid to molybdenum (IV) oxide

After application of the molybdic acid solution onto the pre-treated gold contacts, the molybdic acid was converted to molybdenum (IV) oxide by thermal annealing. First the surface was dried in air for 5 minutes at 120°C and then annealed in air for 5 minutes
30 at 140°C.

Without a tetrathiomolybdate adhesion layer, annealing of molybdic acid on gold resulted in a fast degradation of the surface work function. This is demonstrated by the following example.

35

Example 2**(a) Without an Ammonium Tetrathiomolybdate Adhesion Layer**(I.A) UV-ozone treatment

5 An OTFT substrate comprising gold source and drain contacts on a glass substrate was treated with UV-ozone. This pre-treatment increased the work function of the contacts surfaces to 5.6eV. This is shown in Figure 4 by the label (I.A).

(II.A) Molybdic acid deposition

10 The UV-ozone pre-treated gold surface was then immersed in a 2% (w/w) solution of molybdic acid in water, and blown-dry with a nitrogen gun. The deposition of molybdic acid resulted in a decrease of the surface work function to 5.43eV. This is shown in Figure 4 by the label (II.A).

(III.A) Annealing in air

15 Finally the molybdic acid was converted to MoO_3 by annealing in air; first by drying at 115°C for 5 minutes and then annealing at 140°C for a further 5 minutes. This resulted in a further gradual decrease of the surface work function first to 5.3eV and then to 5.2eV. This is shown in Figure 4 by the label (III.A).

20 (b) With an Ammonium Tetrathiomolybdate Adhesion Layer(I.B) UV-ozone treatment

25 An OTFT substrate comprising gold source and drain contacts on a glass substrate was pre-treated with UV-ozone, immersed in a 0.5% (w/w) solution of ammonium tetrathiomolybdate in water, blow dried with a nitrogen gun and then annealed in air for 10 minutes at 220°C. The resulting ammonium tetrathiomolybdate pre-treated & annealed substrate had an initial work function of 4.8eV. This is shown in Figure 4 by the label (I.B).

(II.B) Molybdic acid deposition

30 The ammonium tetrathiomolybdate pre-treated gold contacts were then immersed in a 2% (w/w) solution of molybdic acid in water, and blown-dry with a nitrogen gun. The deposition of molybdic acid resulted in an increase of the surface work function to 5.43eV. This is shown in Figure 4 by the label (II.B).

35 (III.B) Annealing in air

Finally the molybdic acid was converted to MoO_3 by annealing in air; first by drying at 120°C for 5 minutes and then annealing at 140°C for a further 5 minutes. Upon annealing the surface work function remained fairly stable with a value of 5.43eV after 5 minutes at 120°C and 5.4eV after 5 minutes at 140°C . This is shown in Figure 4.

5

This comparison shows that without an ammonium tetrathiomolybdate adhesion layer, annealing of molybdic acid on gold results in a fast degradation of the surface work function. In contrast, when an ammonium tetrathiomolybdate adhesion layer is used the surface work function during annealing of the molybdic acid remains fairly stable.

10

As a result the present invention has a useful application in the fabrication of temperature-stable ohmic contacts between the organic semiconductor layer and the source and/or drain electrodes within an organic thin-film transistor device.

15

After thermal conversion of the molybdic acid to molybdenum (IV) oxide (MoO_3), the organic semiconductive layer and dielectric layer of the OTFT were deposited thereon, followed by thermal evaporation of the gate electrode. These further steps to produce an organic thin-film transistor in accordance with the present invention can be carried out by any technique known to the skilled man.

CLAIMS

1. Use of an ammonium thio-transition metal complex as an adhesion promoter for immobilising temperature-stable transition metal oxide layers on an inert metal surface.
2. The use according to claim 1 wherein the ammonium thio-transition metal complex comprises a transition metal selected from molybdenum, tungsten and vanadium.
3. The use according to claim 1 or claim 2 wherein the ammonium thio-transition metal complex is a tetrathio-transition metal complex.
4. The use according to claim 3 wherein the ammonium tetrathio-transition metal complex is ammonium tetrathiomolybdate.
5. The use according to any one of claims 1 to 5 wherein the transition metal oxide is MoO_3 , WO_3 or V_2O_5 .
6. The use according to any one of claims 1 to 5 wherein a precursor of the transition metal oxide is deposited on the inert metal surface by a solution-based process.
7. The use according to claim 6 wherein the precursor is a dispersion or a dissolution of the transition metal oxide, transition metal oxide hydrate, ammonium salt of an acidic transition metal oxide hydrate or phosphoric acid-transition metal oxide complex in water or a phosphoric acid-transition metal oxide complex dissolved in a polar organic solvent.
8. The use according to claim 7 wherein the transition metal oxide to be deposited is MoO_3 and the precursor is a dispersion or a dissolution of molybdenum trioxide, molybdic acid, ammonium molybdate or phosphomolybdic acid in water, or phosphomolybdic acid dissolved in a polar organic solvent.

9. The use according to claim 7 wherein the transition metal oxide to be deposited is WO_3 and the precursor is a dispersion or a dissolution of tungsten trioxide, tungstic acid, ammonium tungstate or phosphotungstic acid in water, or phosphotungstic acid dissolved in a polar organic solvent.
- 5
10. The use according to claim 7 wherein the transition metal oxide to be deposited is V_2O_5 and the precursor is a dispersion or a dissolution of vanadium (V) oxide, ammonium metavanadate, vanadium(V) oxytriethoxide vanadium(V) oxytriethoxide, vanadium(V) oxytriisopropoxide or vanadium(V) oxytripropoxide
- 10 dissolved in a polar organic solvent.
11. The use according to any one of claims 6 to 10 wherein the solution-based process consists of spin-coating, dip-coating or inkjet-printing.
- 15
12. The use according to any one of claims 1 to 11 wherein the inert metal is silver, gold, or copper.
13. The use according to claim 12 wherein the inert metal is gold.
- 20
14. The use according to any one of claims 1 to 13 wherein the transition metal oxide layer immobilised on the ammonium thio-transition metal complex is stable up to temperatures of at least 140°C .
- 25
15. A process for forming a transition metal oxide on an inert metal surface comprising:
- (a) pre-treating the metal surface with an ammonium thio-transition metal complex;
- (b) depositing a solution comprising a transition metal oxide precursor onto the pre-treated surface; and
- 30 (c) annealing the deposited solution to form a layer of transition metal oxide.

16. A process according to claim 15 wherein step (a) comprises:
- (i) cleaning the metal surface to remove organic contaminants;
 - (ii) depositing the ammonium thio-transition metal complex onto the metal surface; and
 - 5 (iii) annealing of the treated surface in air.
17. A process according to claim 16 wherein the metal surface is cleaned by a UV-ozone treatment or an oxygen plasma treatment.
- 10 18. A process according to any one of claims 15 to 17 wherein the solution-based deposition is conducted by spin-coating, dip-coating or inkjet printing.
- 15 19. An organic thin-film transistor comprising source and drain electrodes, a gate electrode and an organic semiconductor layer, wherein the source and drain electrodes comprise an inert metal on which a temperature-stable transition metal oxide layer is immobilised by use of an ammonium thio-transition metal complex as an adhesion promoter.
- 20 20. An organic thin-film transistor according to claim 19 wherein the transition metal oxide is immobilised according to the process defined in any one of claims 15 to 18 above.
- 25 21. An organic thin-film transistor according to claim 19 or 20 wherein the ammonium thio-transition metal complex is as defined in any one of claims 1 to 4 above.
22. An organic thin-film transistor according to any one of claims 19 to 21 wherein the transition metal oxide is MoO_3 , WO_3 or V_2O_5 .

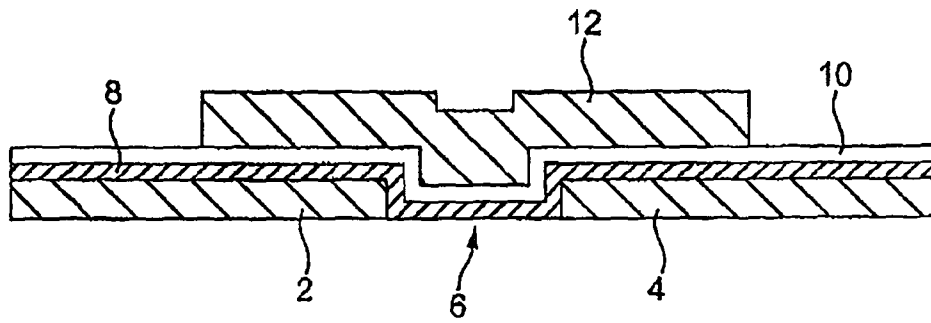


FIG. 1

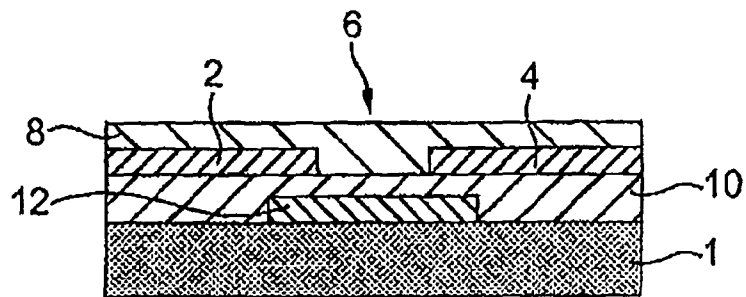


FIG. 2

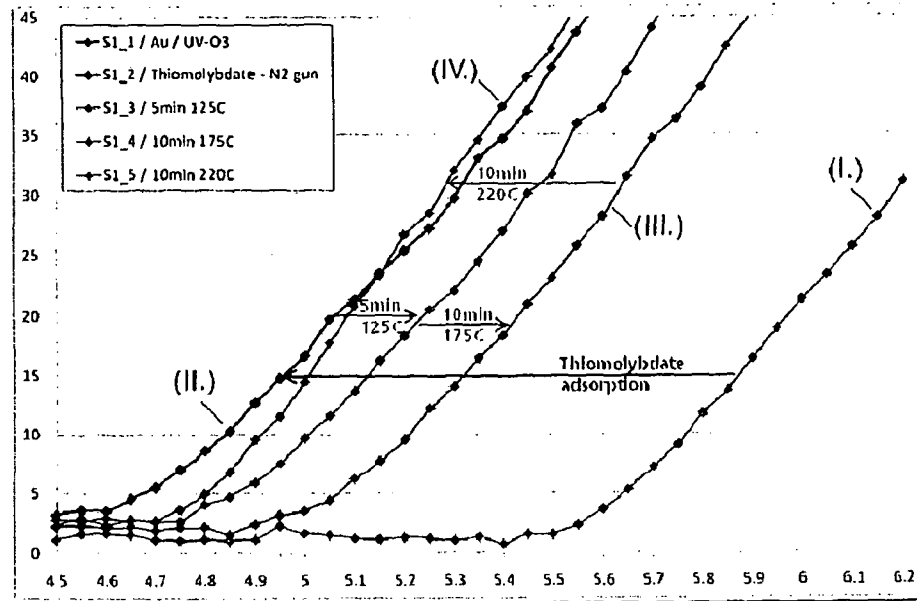


FIG.3

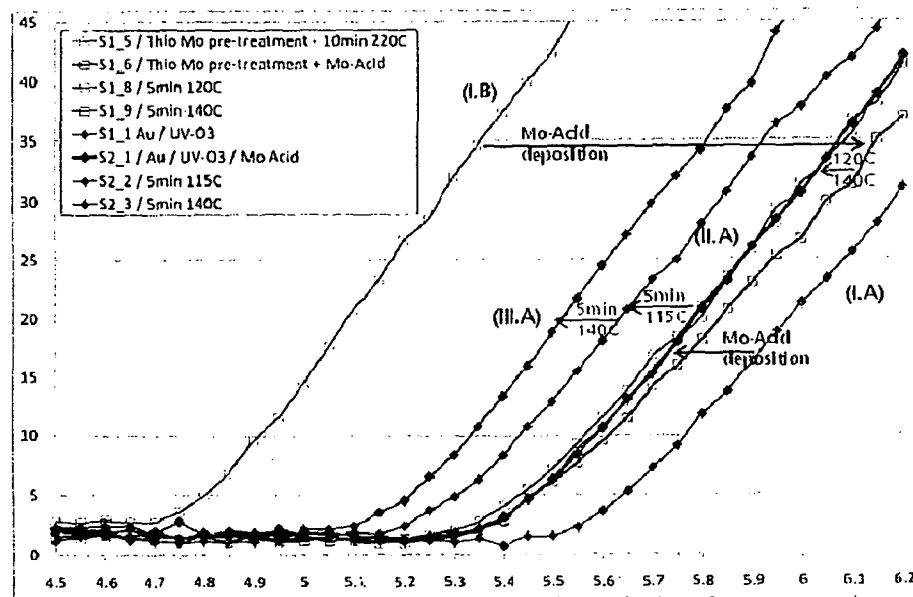


FIG.4

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/001667

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C18/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 777 058 A1 (TOYOTA MOTOR CO LTD [JP]; NIHON PARKERIZING [JP]) 4 June 1997 (1997-06-04) cited in the application the whole document -----	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

15 March 2012

Date of mailing of the international search report

27/03/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ramos Flores, Cruz

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/001667

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0777058	A1	04-06-1997	
		DE 69613323 D1	19-07-2001
		DE 69613323 T2	18-04-2002
		EP 0777058 A1	04-06-1997
		US 5879816 A	09-03-1999
